RETROSPECTIVE ANALYSIS OF NECOP AREA SEDIMENTS: BIOGENIC, INORGANIC AND ORGANIC INDICATORS OF ANTHROPOGENIC INFLUENCES SINCE THE TURN OF THE CENTURY

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Abstract

Surface and cored sediments from the NECOP study area were analyzed for physical (coarse-grain texture, composition), biological (foraminifera) and chemical (organic and inorganic) properties. Results of analyses for surface samples indicated spatial patterns of benthic foraminifera dictated by sediment accumulation rate and regions of seasonal hypoxia. The latter also correlated well with the distribution of surface authigenic glauconite. Temporal variability, determined from core samples, indicated transitions in benthic foraminifera community structure with upcore increases in hypoxia tolerant assemblages. Transitions in glauconite abundance, organic carbon, and other chemical parameters strongly correlated temporally with increases in fertilizer application in the United States.

Introduction.

The Mississippi River basin drains approximately 41% of the contiguous United States and with it comes the byproducts of both natural continental weathering and anthropogenic activities. Basinwide, these signals coalesce and transition seaward entering the Gulf of Mexico at two point sources, the Mississippi Birdfood Delta and the mouth of the Atchafalaya River. With the development of farming in America's heartland, agricultural runoff has also been transported seaward and perhaps the most significant has been enhanced nutrient loading, primarily as a byproduct of man's increasing use of artificial fertilizer. Recent measurements of Mississippi River water indicate rising levels of nutrient concentrations and fluxes (Bratkovich and Dinnel, 1992) that are implied to result from agricultural sources. Within the Louisiana/Texas continental shelf, recent observations of declining water quality have suggested linkage between river and continental shelf water qualities. To test this, the NECOP Program's central hypothesis was formulated to address this potential linkage, specifically:

Hypothesis: *ANTHROPOGENIC NUTRIENT INPUTS HAVE ENHANCED COASTAL OCEAN PRODUCTIVITY WITH SUBSEQUENT IMPACTS ON COASTAL OCEAN WATER QUALITY AND YIELDS OF LIVING RESOURCES.*

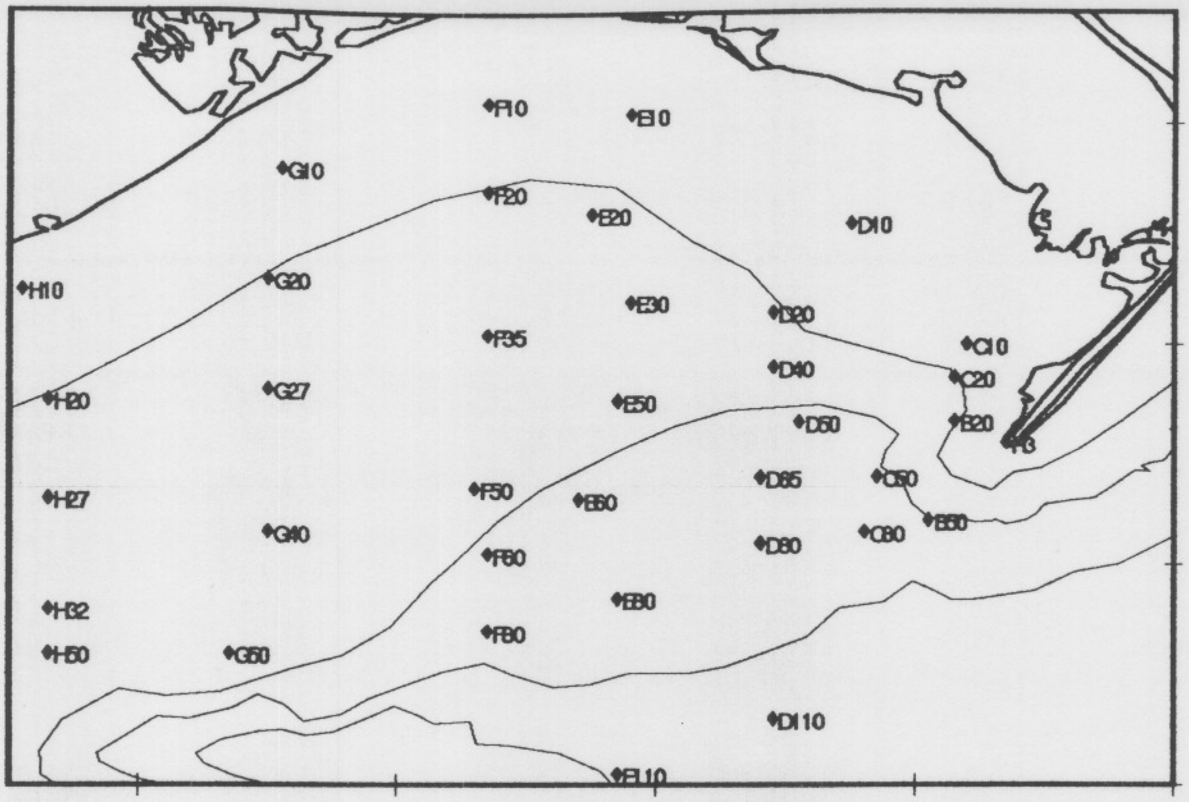
Unfortunately, measurements of Mississippi River water quality only go back for a few decades and coastal water quality less than a decade, and as such fall short of the time history of continental agricultural influences. The sediments however can potentially provide a record over decadal to century time scales and therefore act in a manner analogous to a long time-series record of natural and anthropogenic influences. Within the Louisiana shelf environment, this has been conclusively shown for anthropogenic lead (Trefry et al., 1984). To assist in addressing the NECOP central hypothesis, the Retrospective Analysis Group has tested the following hypotheses relative to the sediment record:

Hypothesis 1: *COMMUNITY STRUCTURE - OBSERVED RIVERINE NUTRIENT ENHANCEMENT, TOGETHER WITH SILICON DECLINE, HAS PROMOTED A SHIFT IN THE BENTHONIC COMMUNITY STRUCTURE OF THE MISSISSIPPI/LOUISIANA SHELF AND THIS SHIFT IS PRESERVED IN THE SEDIMENT RECORD.*

Hypothesis 2: *HYPOXIA INDICATORS - BY-PRODUCTS OF HYPOXIA/ANOXIA EVENTS HAVE LEFT CHARACTERISTIC MARKERS WHICH PRODUCE A TIME HISTORY OF SUCH EVENTS IN THE SEDIMENT RECORD.*

Hypothesis 3: *CARBON ACCUMULATION ANTHROPOGENIC NUTRIENT ENHANCEMENT IN THE COASTAL ZONE HAS PRODUCED PROPORTIONAL ENHANCEMENT OF PRIMARY PRODUCTIVITY AND CONCOMITANT CARBON BURIAL IN THE SHELF SEDIMENT DEPOCENTERS.*

A



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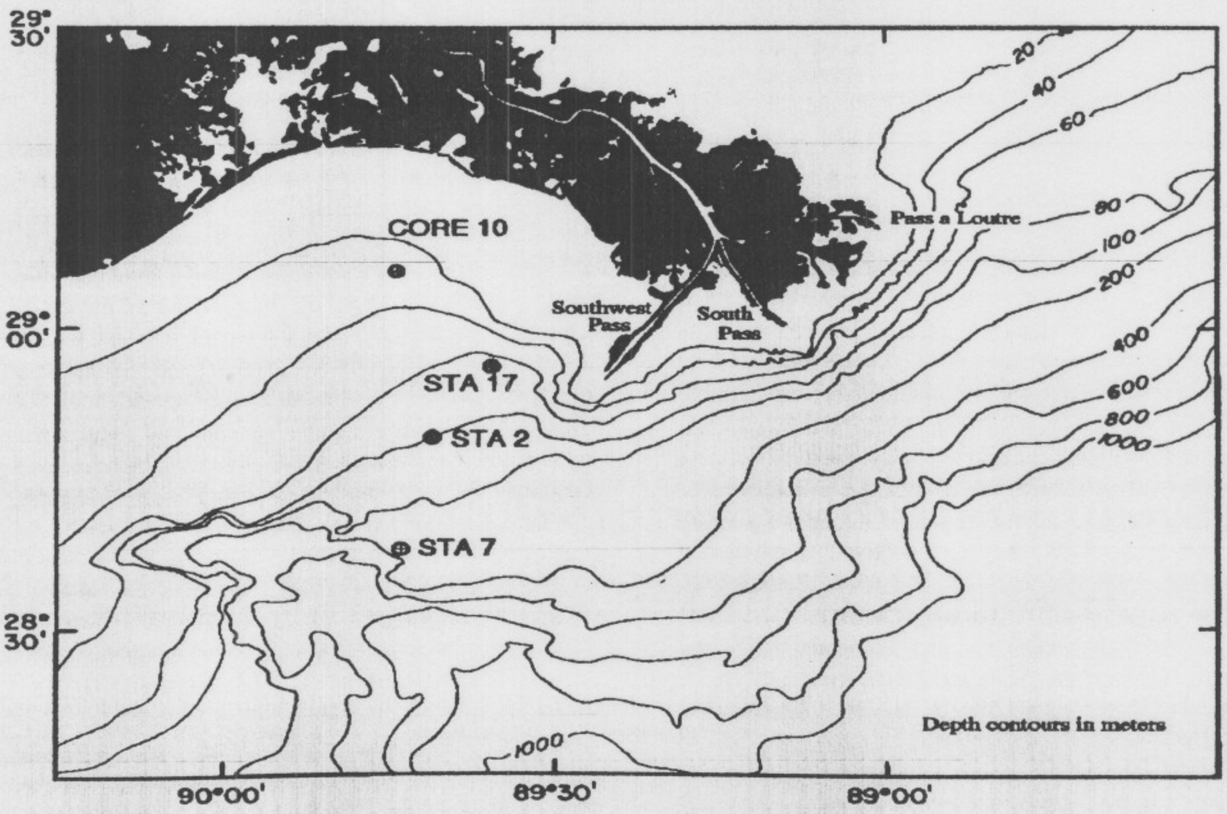

Fig. 1. A. Locations of surface grab samples examined in the study, B. Locations of cores recovered and analyzed in this study.

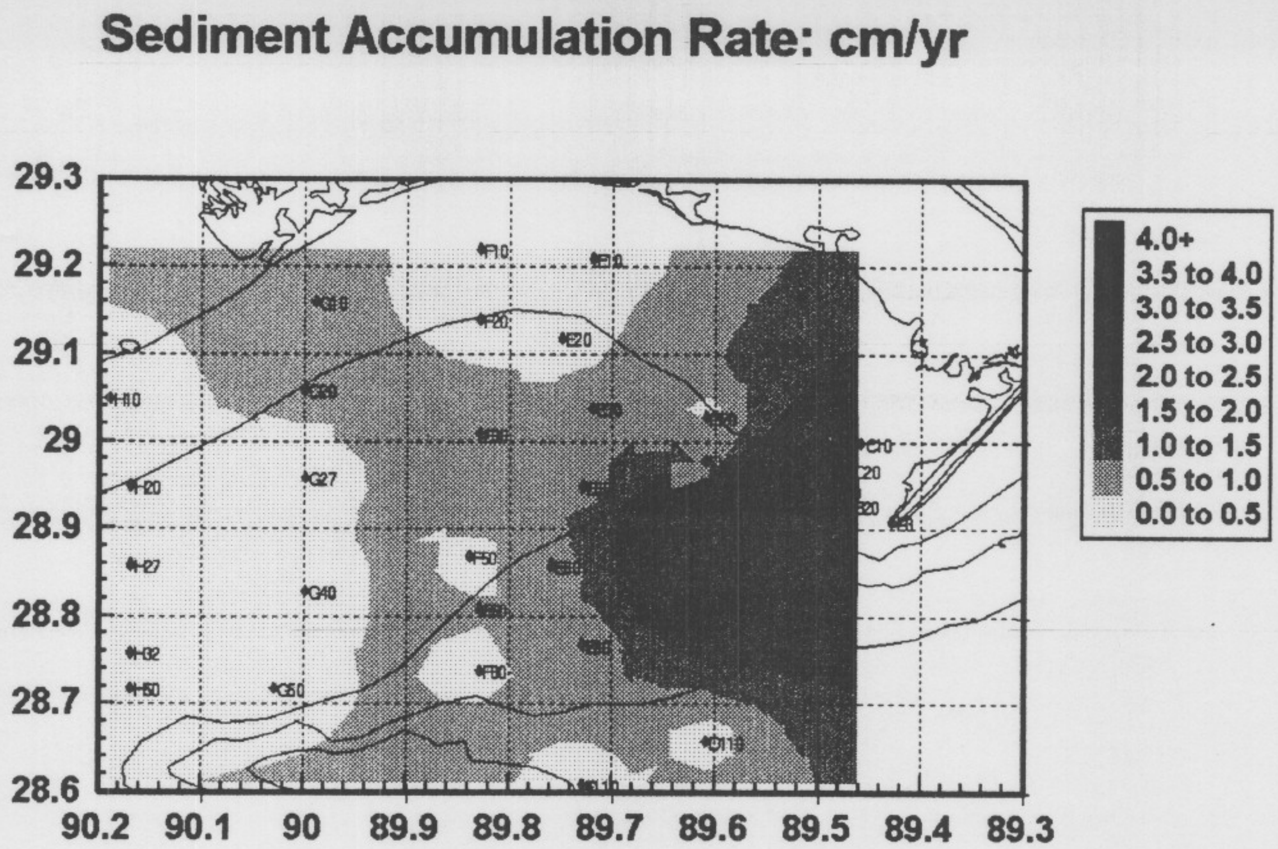

Fig. 2. Surface sediment accumulation rates (cm yr^{-1}) determined during the LASER Program.

Our progress to date, in testing these hypotheses, will be reported for both surface and cored sediments. The locations of surface sediment grab samples are shown in Fig. 1A and cored sediments in Fig. 1B.

Surface Sediments.

The grab-sample network (Fig. 1A) occupies prior LASER sites for which sediment accumulation rates have already been measured. The collection of surface sediments had the goal of evaluating the most recent sediment record for comparison to current environmental conditions such as sediment accumulation rates and seasonal hypoxia. The overall objective however was to take the results of these comparisons and apply them to downcore trends under the premise that "the present is a key to the past". Investigated parameters included benthic foraminifera distributions, organic carbon and glauconite distribution.

Sediment accumulation rate patterns reflect the large input from the Mississippi River, specifically from Southwest Pass, as shown in Fig. 2. The highest accumulation rates (4 cm yr^{-1}) are not directly adjacent to Southwest Pass but westward and centered at ~89.6 W and ~28.9 N. From this major depocenter, accumulation-rate gradients decline steeply to <1 cm yr^{-1} over most of the study area.

To test our hypothesis concerning benthic community structure in the sediment record, and its shift with time, if any, we studied the foraminifera community at each grab site (Fig. 1A). Approximately 300 benthic and planktic foraminifera were picked for each station and identified to the species level. In order to evaluate shifts in benthic foraminifera biodiversity, the Shannon-Wiener Information Function was utilized (Patrick, 1983). This index incorporates a measure of species evenness as well as number of species such that communities with many species of equal-size populations have the highest index. The index of diversity (H) is computed from the following expression:

$$H = -\sum_{i=1}^{N} p_i \ln p_i$$

where N is the number of species, and p_i is the proportion of the total number of individual species which belong to the i^{th} species (MacArthur, 1983). In

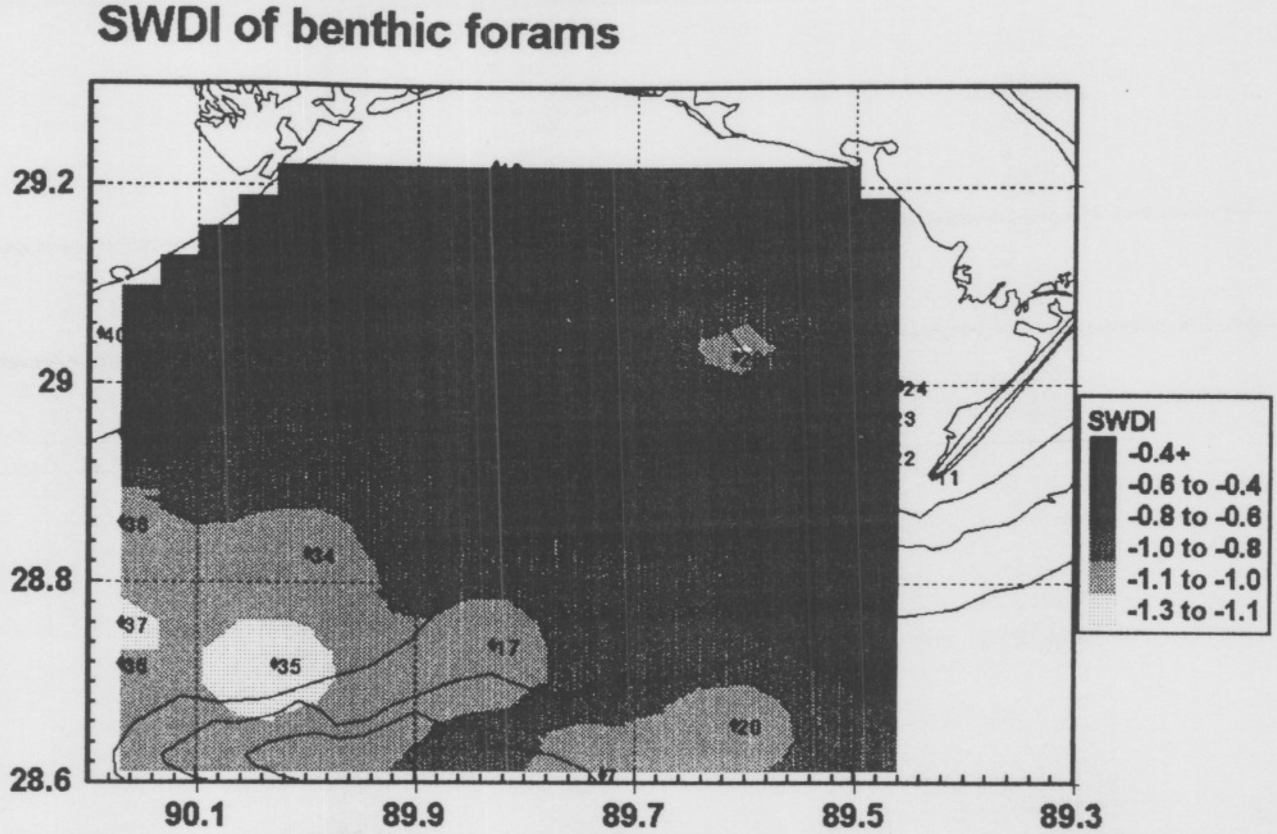

Fig. 3. Map of the diversity (SWDI, see text) of benthic foraminifera from the surficial sediments in the study area. Lower values (e.g. -0.4) indicate lower foraminifera-community diversity and visa versa.

this text, H will be referred to as the Shannon-Wiener Diversity Index (SWDI). Smaller values (e.g. -0.4) indicate lower diversity and visa versa.

Results indicate that the lowest values of the SWDI (Fig. 3) coincide with sediment accumulation-rate highs (Fig. 2) thus suggesting that diversity may be strongly influenced by sedimentation patterns. Spatial plots of all the identified foraminifera species indicated only a coherent pattern between accumulation rates and Epistominella vitrea (Fig. 4). As suggested by comparison of this distribution and that of sediment accumulation rate (Fig. 2), Epistominella vitrea strongly correlates ($r = 0.69$, $n = 38$) with sediment accumulation rate indicating a tolerance for such environmental conditions. Although spatial coherence between accumulation rates and Epistominella vitrea is high, the relatively low abundance of this species along the northern edge of the study area cannot help account for the relatively low SWDI values in this region.

Comparison of the surface distribution of the benthic foraminifera Buliminella morgani (Fig. 5) with sediment accumulation rate patterns (Fig. 2) show low correlation ($r = 0.01$, $n = 38$) indicating that the distribution of Buliminella morgani is not directly controlled by this process. However, the areas where Buliminella morgani comprise the dominant (i.e. ~50>65%) species of the foraminifera population corresponds to the highest occurrences of hypoxia (i.e. 69 out of nine years, Fig. 6) while offshore, where hypoxia has never been observed, Buliminella morgani percentages rapidly diminish. As such, these data clearly establish the present-day association between the benthic foraminifera Buliminella morgani and seasonally hypoxic environments.

In addition to community structure, we tested our hypothesis on characteristic markers of hypoxia/anoxia within the sediment and found evidence which supported the trends established by benthic foraminifera. During microscopic analysis of the 63μm fractions, a grain type was observed whose very-high abundance was limited to the 63μm fraction. These grains exhibited coloration in various shades of green and ranged from 63-200μm in diameter. Initial chemical analysis indicates a composition consistent with the solid-phase glauconite. Analyses, using SEM/EDA, indicate a major-element composition of Si, Al, Fe, K,

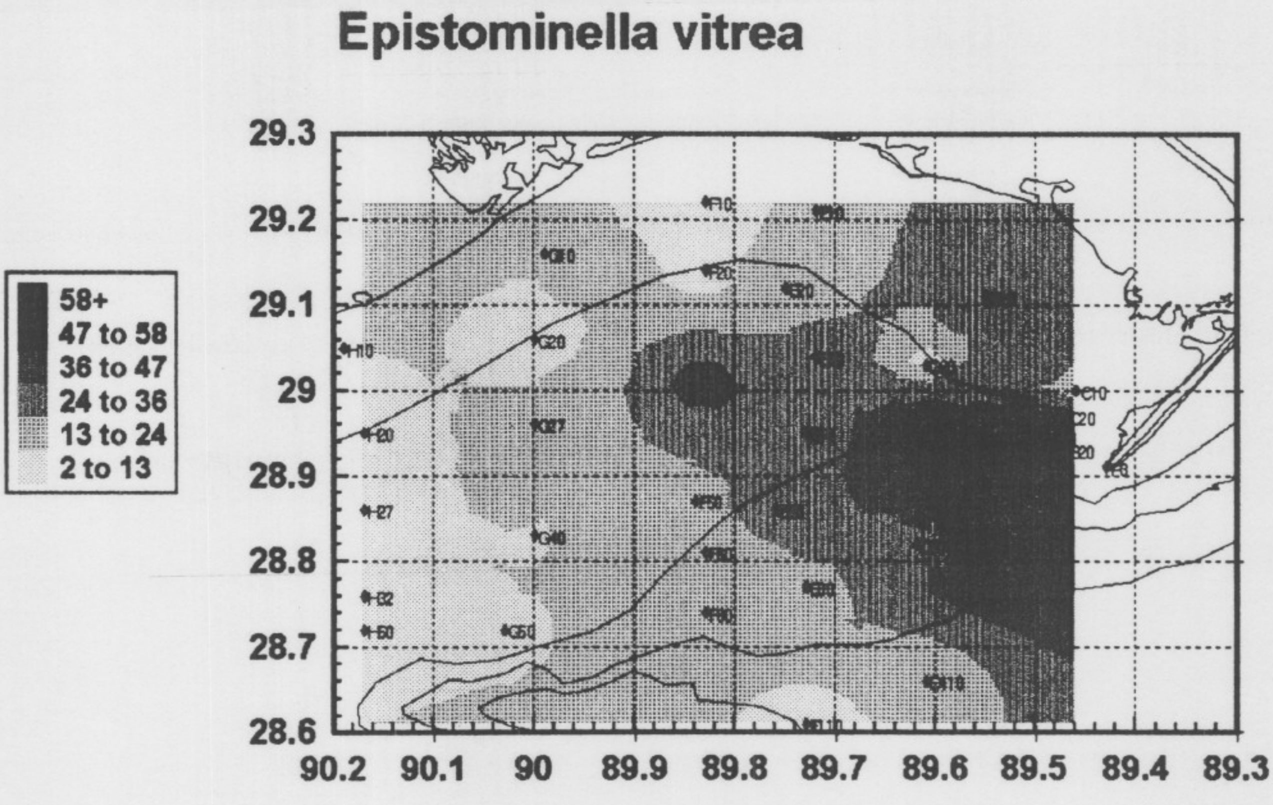

Fig. 4. This figure illustrates the surface distribution of the benthic foraminifera Epistominella vitrea expressed as percentage of the total benthic foraminifera population in each station sample.

and Mg, which corresponds well with the known major element composition of glauconite, which has the general formula of :

$K_{(x+y)}(Si_{4-x},Al_x)_{-4}(Fe^{+3}Al,Mg,Fe^{+2})_{-2}O_{10}(OH)_2$ (Odin, 1988)

This ongoing chemical and physical study of glauconite, from the shelf region adjacent to the Mississippi River, is based on our network of grab samples (38) uniformly covering the area of Fig. 7 as well as at the Mississippi River mouth and upriver (Hood et. al, in prep). Results to present indicate that shelf glauconite is chemically and physically (size) distinct from the river-borne population and enriched in Fe, Mg, and K relative to normal shelf sediments. Moreover, comparison of this figure with Fig. 6 indicates the highest percentage of surface glauconite is observed in areas of documented hypoxia (Nelsen et al., 1994). Glauconite grain-size-distribution data indicate that the river-derived component accounts for only 15%. The latter observation implies that while changes in discharge, channelization, and damming of the Mississippi River may induce modifications in the detrital fraction of glauconite present on the shelf, such would constitute a only a minor change in the current population.

Surface sediment concentrations of organic carbon range from 0.57% at station H-10 (nearshore at western edge of sample grid) to 1.91% at station F-10 (nearshore northern edge of grid at ~89.8 N). For comparison, Mississippi River suspended matter averages about 1.5-1.8% organic carbon. The trend for organic carbon values, seen in Fig. 8, shows a path of more organic-rich sediments along an hypothesized transport pathway from the mouth of Southwest Pass to the northwest as observed during lagrangian drifter studies. Lower levels of organic carbon to the west are found in somewhat coarser-grained sediments. Trends for sediment N and P are comparable with those for organic carbon.

Cored Sediments.

While surface samples allow spatial relationships to be evaluated, age-dated cores provide the temporal context of primary interest to the NECOP Program. Coring objectives were to recover interpretable sedimentary sequences from both the areas of seasonal hypoxia and areas outside the seasonal hypoxia. The former allowed study of time history of hypoxia indicators while the latter provided a control condition for comparison. Investigated parameters included coarse-fraction (>63μm) abundances of quartz,

Buliminella morgani

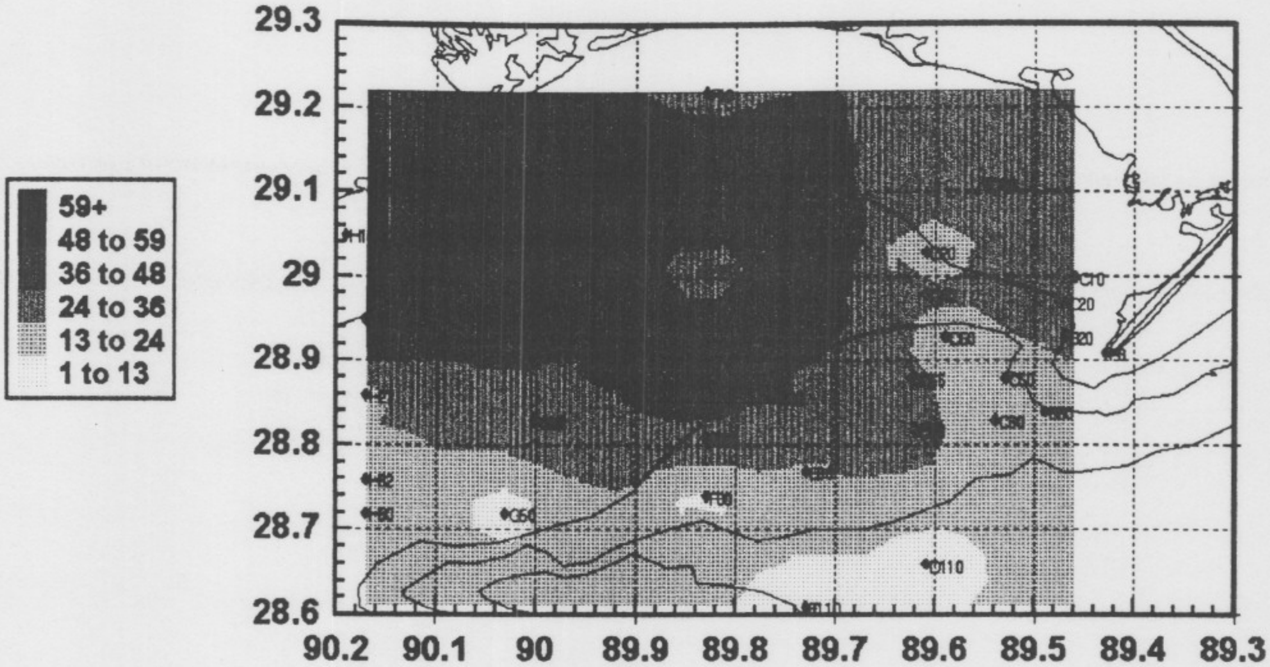

Fig. 5. This figure illustrates the surface distribution of the benthic foraminifera Buliminella morgani expressed as

Hypoxia Frequency: 1985-1993

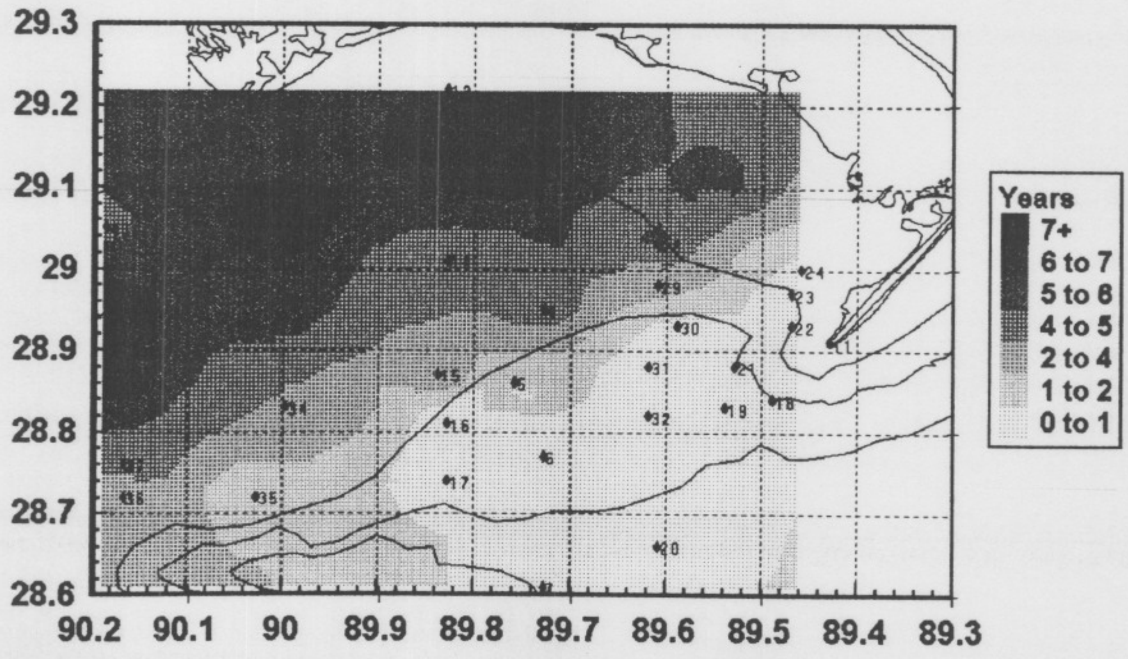

Fig. 6. These data illustrate the frequency and distribution of hypoxia that has occurred at each sampling station over approximately the last decade (1985-1993) based on existing hypoxia monitoring data (N. Rabalais, personal communication and seasonal hypoxia distribution maps).

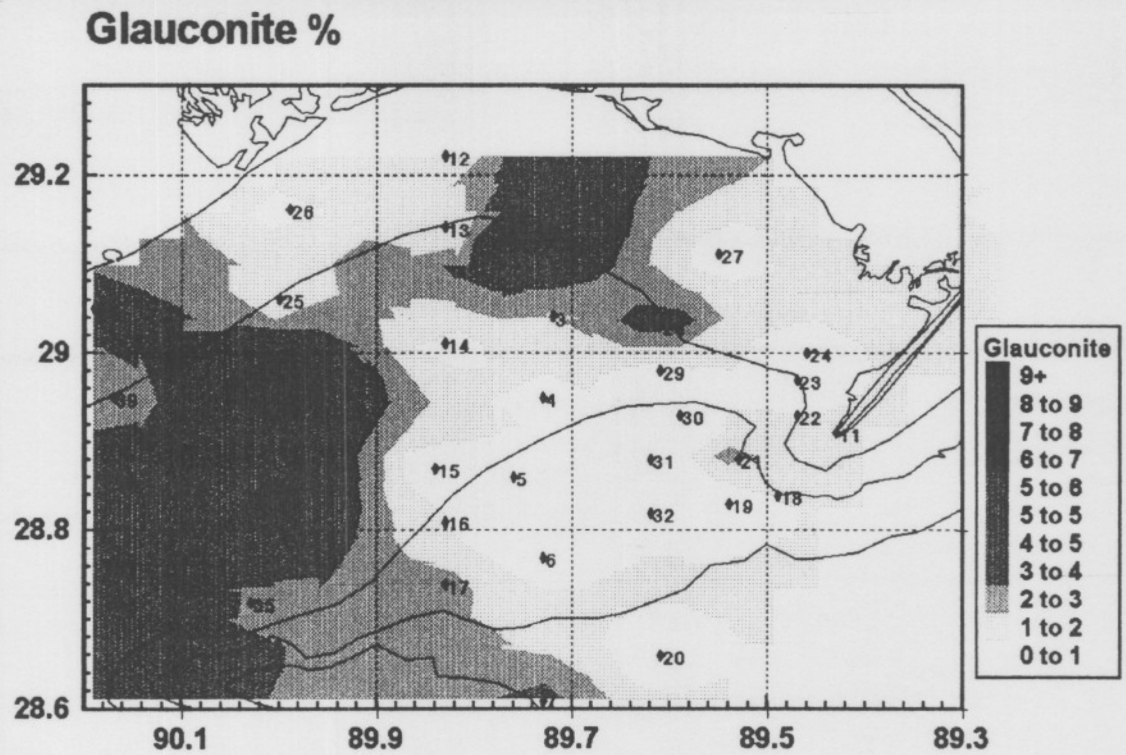

Fig. 7. The surficial distribution of authigenic glauconite expressed as a percentage of the coarse (63m) sediment fraction.

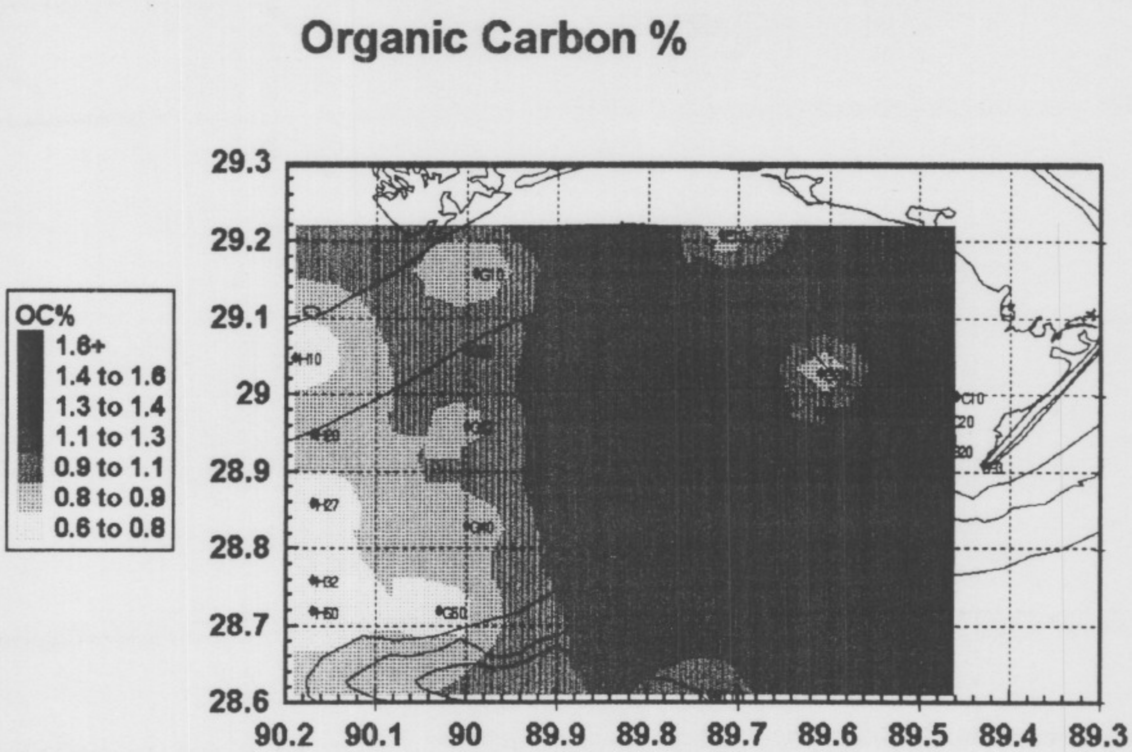

Fig. 8. A contour map showing concentrations of organic carbon (%) in surficial sediments (0-2 cm) from the Louisiana continental shelf.

glauconite, and benthic foraminifera community composition, community shifts and diversity changes as well as organic carbon, stable carbon isotopes and organic tracers. These parameters provided a data base for understanding environmental changes from ~1900~1990.

Core site selection was based on two criteria: 1) areas known for the presence and absence of documented seasonal hypoxia and, 2) a region in which sediment accumulation rates are adequate to allow decadal to century time-scale resolution. Sediment geochronology was done by ^{210}Pb to both establish an intact and interpretable sedimentary sequence and, once established, provide a temporal framework for subsequent analyses.

Core 10 (Fig. 1B) is the closest to a distributary mouth (~33 km), and in an area of documented persistent seasonal hypoxia (Rabalais et al., 1991). A sediment accumulation rate of 0.55 cm yr^{-1} (i.e. Fig. 9A: 1 cm 2 years) at this core site allowed analysis back to about the turn of the century. Thus, it was ideal for observing changes, if any, in sediment components due to anthropogenic influences during the last ~90 years. The Station 7 core was recovered near the shelfedge ~42 km from the mouth of S.W. Pass (Fig. 1B). It has an established geochronology of ~1900-1980 (Fig. 9B) and was therefore ideal for comparison of non-hypoxic (Station 7) with seasonally-hypoxic (Core 10) shelf conditions since just after the turn of the century.

Detailed (1 cm intervals) analysis of the sediment's coarse fraction (63m) indicated a complex and variable record of quartz within Core 10 (Fig. 10A). A linear trend analysis of these data indicates an upcore decline (~8267%) in lithogenic quartz abundance that is consistent with declining trends of sand transport for the Mississippi River (Meade and Parker, 1984). In contrast, the total coarse fraction displays an increasing upcore trend (Fig. 10A) indicating that the abundance changes of this portion of total sediment is controlled by factors other that lithogenic quartz.

A plot of glauconite abundance in Core 10 (Fig. 10B), along with a linear trend analysis of these data, indicates an upcore increase in this component consistent with the trend in total coarse percent and antithetical to the lithogenic quartz trend (Fig. 10A vs B). Conditions at the Core 10 site are known to be favorable for authigenic glauconite (glaucony/verdine facies: shallow marine, free access to sea water, and a sediment rich in constituent elements). Studies of the geologic record document the close association of glauconitization episodes and anoxic episodes in shelf settings (Bréhéret, 1991). Moreover, we believe compelling evidence exists for the role of anthropogenic input in enhancing the formation of hypoxia with

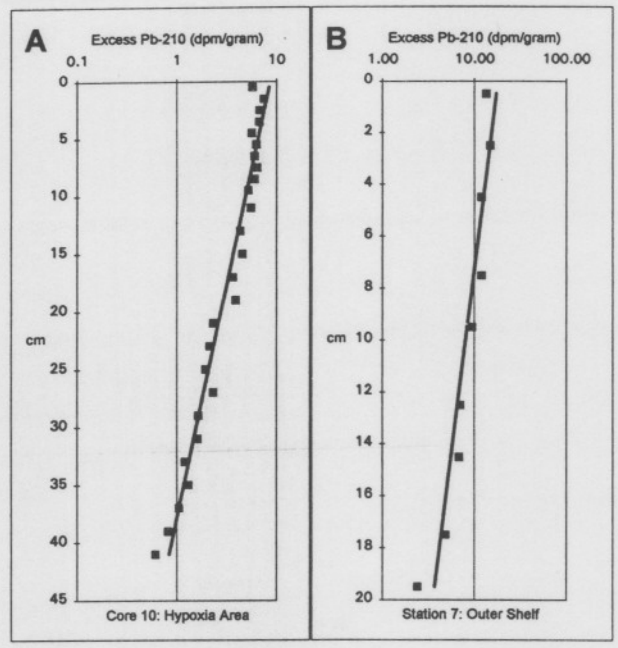

Fig. 9. Excess ^{210}Pb curves for: A. Core 10 from an area of chronic seasonal hypoxia, B. core at Station 7 on the outer shelf and not in an area of documented seasonal hypoxia.

concomitant formation of authigenic glauconite in Core 10. This is suggested by a transitional increase of ~2.3x in mean glauconite abundance after the late-1930's to early-1940's time horizon (Fig. 11A, arrow). Specifically, below the transition, average glauconite abundance accounts for ~5.8% of the coarse fraction while above this horizon it accounts for ~13.4%.

Our study of benthic foraminifera from Core 10 augments and confirms trends and interpretations based on glauconite data as will be shown next. Evaluation, using both light and electron microscopy, indicates that post-depositional processes have not altered the benthic foraminifera tests in Core 10. Therefore, detailed identification and trend analysis was feasible down to core base (~1900) for both total foraminifera abundance and species identification. Relative to the former, Fig. 10B contains a plot of foraminifera abundance and a linear trend analysis for these data. As with glauconite data, an upcore increase mimics the increasing coarse percent trend and is also antithetical to the lithogenic quartz trend (Fig. 10A). In addition, a total of 49 benthic foraminifera species were identified from seven levels in this core. Contrasting trends of upcore species composition variability emerged. One assemblage, Epistominella vitrea, Buliminella morgani, Brizalina lowmanii, Nonionella atlantica, Nonionella opima and Ammonia parkinsoniana tepida (referred to hereafter as

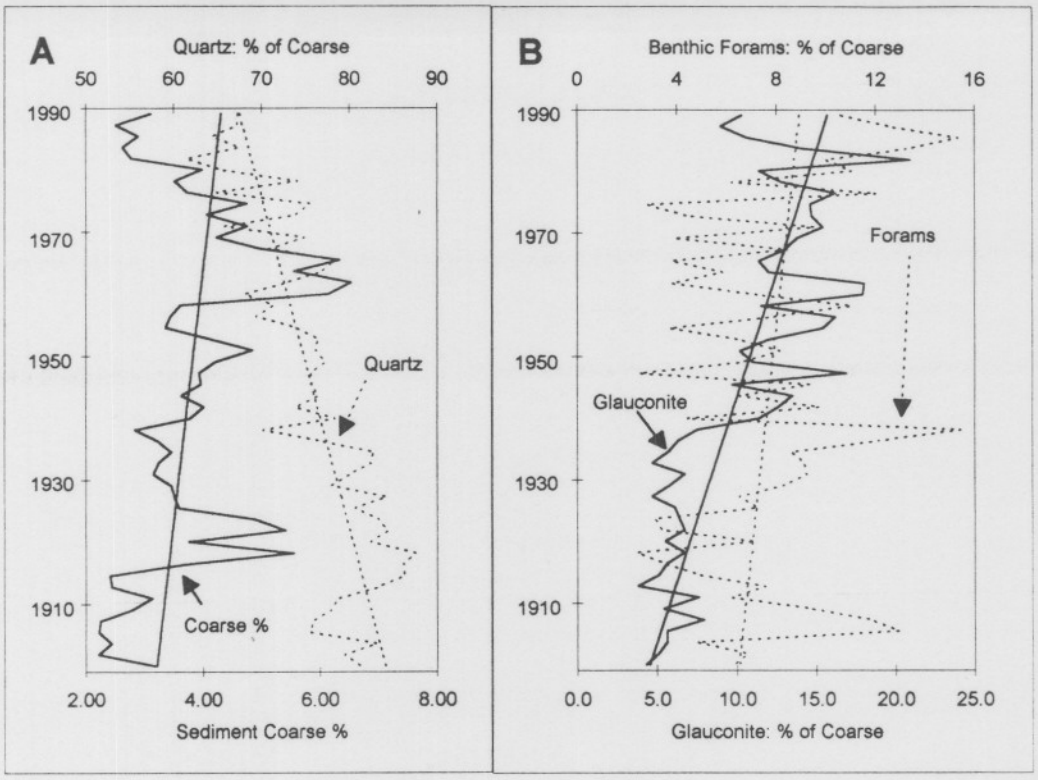

Fig. 10. Distribution and trends of sediment coarse (63m) fraction components in Core 10 showing: A. total coarse fraction (solid) and quartz (dashed), and B. glauconite (solid) and benthic foraminifera (dashed).

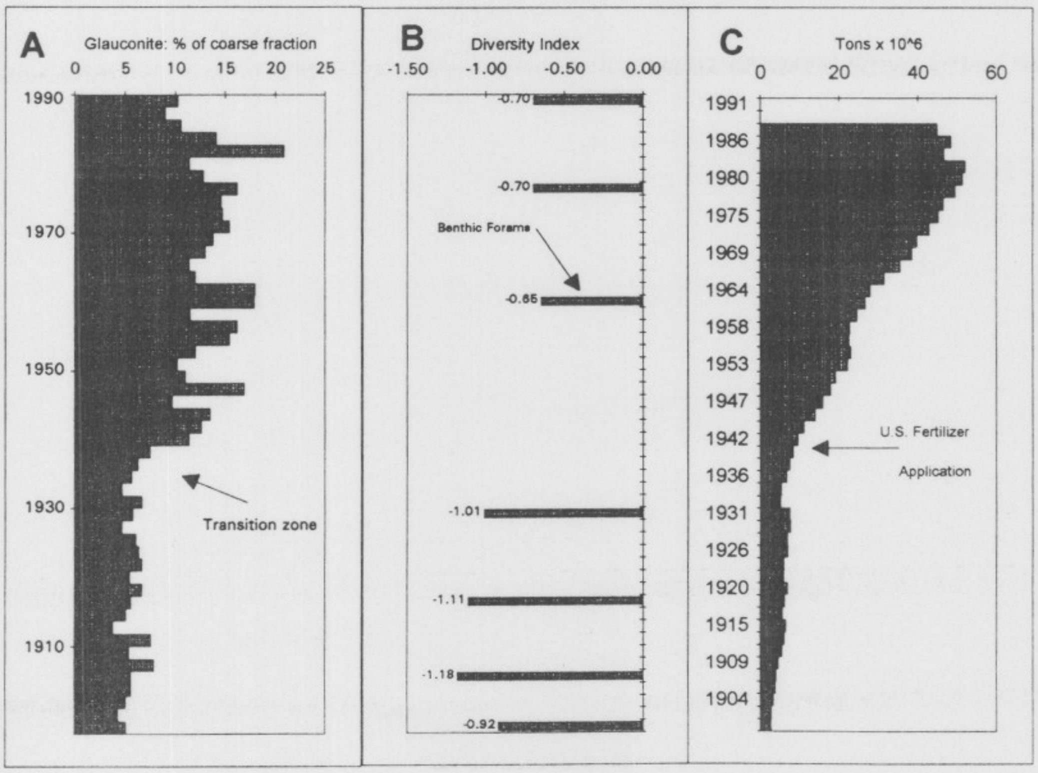

Fig. 11. A. Glauconite grain abundance, B. the Shannon-Wiener Diversity Index for benthic foraminifera for Core 10 compared to: C. the application of fertilizer in the United States for the years 1900-1990.

Group A), displayed an upcore increase in group abundance, as a percentage of total foraminifera species, from 52% at 42-43 cm (~1910) to 90% at 3-4 cm (mid-1980's). Group A was dominated by hypoxia-tolerant E. vitrea and B. morgani which changed from 22% and 27% (= 49%) at core bottom, to 15% and 58% (= 73%) at core top, respectively. In contrast to this, agglutinated, miliolid and hypoxia-intolerant hyaline foraminifera species (Group B) decrease upcore. Specific upcore decreases, as a percentage of total foraminifera population, are: 1) agglutinated - 17% at 42-43 cm (~1910) to 1.5% at 3-4 cm (mid-1980's), 2) miliolids - 9% at 42-43 cm to 1.1% at 3-4 cm, 3) hypoxia-intolerant hyaline - 17% at 42-43 cm to 7% at 3-4 cm.

The ostracodes are an additional benthic population of interest in Core 10. This group is known to be sensitive to variability in environmental parameters such as salinity, temperature, substrate, and availability of food supply (Athersuch et al., 1989). Preliminary results of our study of Core 10 indicate that diversity as well as population abundance of ostracodes decreases upcore (Alvarez-Zarikian et al., in prep.). These findings suggest that the ostracode population may be more sensitive than the foraminifera to the onset of hypoxia, and is an important potential indicator of historical low-oxygen conditions.

The significance of these population changes is evident when compared to the current surficial distributions of these same species, and their environmental settings. Considerable environmental insight has been gained from contemporary distributions of the foraminifera species in Groups A and B, obtained from the surface grab samples, which is relevant to Core 10. Detailed comparisons of areas of documented hypoxia and surficial distribution of foraminifera indicate that Group A species dominate the hypoxic-area populations. In contrast, members of Group B are either absent or form a very-minor component of hypoxia-area samples. The latter become more abundant in better oxygenated areas. In general, the foraminifera assemblage observed in the lower portion (>25 cm, early-1940's) of Core 10 resembles that from non-hypoxic area surface grab samples. In contrast, near core top, the assemblage is similar to that observed in surficial samples from hypoxic areas. In order to examine quantitatively the extent to which the benthic foraminifera population may have changed over time, the SWDI was calculated for each of the seven levels examined in Core 10. The results, shown here in Fig. 11B indicate that the diversity decreases from near -1.0 at core base (~1900) to -0.70 at the core top (~1991). The greatest change occurred between 1930 and 1960. It has been established in previous studies that variation in

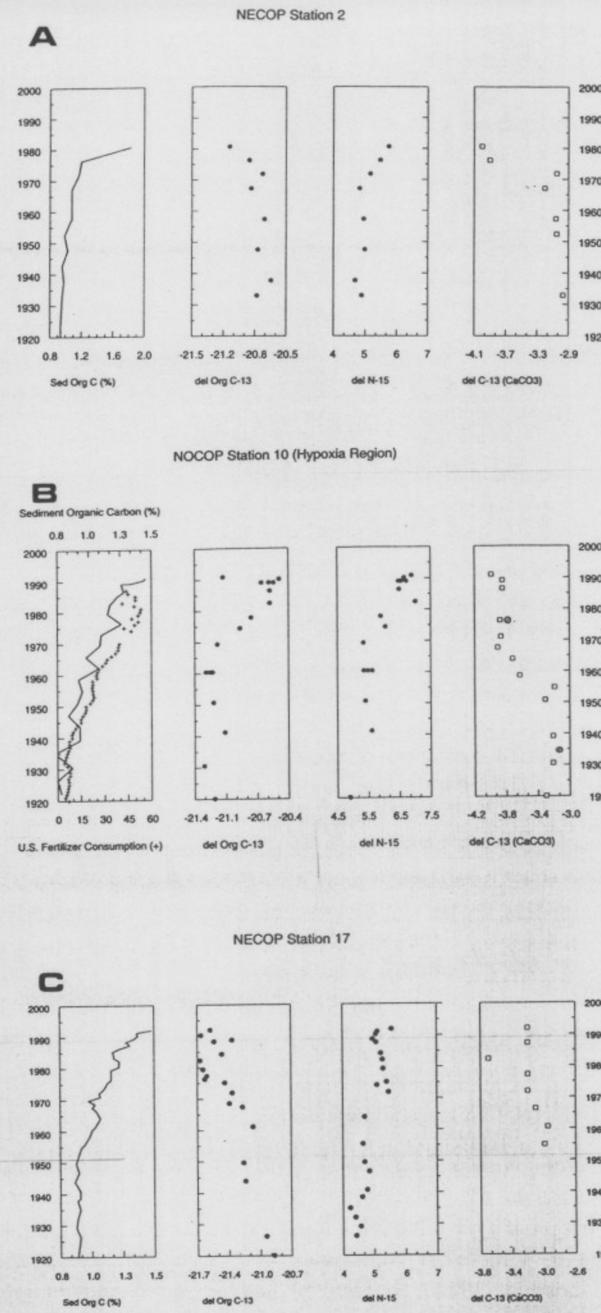

Fig. 12. Organic chemical data for: A. NECOP station 2, B. NECOP Core 10, and C. NECOP station 17.

population diversity can be used to measure the degree of perturbation by man (Patrick, 1983). Therefore, we believe that the water quality variability (i.e. hypoxia) plays a role in our observations. This was independently confirmed by in-depth observations of organic-carbon and nitrogen chemistry in Core 10 and other cores within the study area which will be presented next.

Surface organic carbon concentrations (first panel, Figs. 12A-C) were greater than 1.3%, similar to previously reported values for the northern Gulf shelf (Shokes, 1976; Entzeroth, 1982) and throughout the record of this century until a relatively constant background level of approximately 0.8% is reached below a depth corresponding to approximately 1945.

The organic carbon isotope ratio data is shown in the second panel for each core (Figs. 12A-C). The surface intervals are isotopically light and may be contaminated or contain materials (such as labile, isotopically light lipids) that are rapidly remineralized near the sediment-water interface, and thus are not characteristic of the materials that are eventually consolidated. Below the first cm, the ^{13}C values from Core 10 are heavier (more marine) near the surface, then get lighter downcore to a relatively constant value below the early 1960s horizon. The overall downcore change in ^{13}C is small, less than 1‰, but real. Triplicates (split sediment samples) of three depths for Core 10 and two depths for station 2 provide an average standard deviation of 0.06 ‰. The decrease in ^{13}C at Core 10 (within the region of recurrent hypoxia) is larger than that of station 2. At this station the ^{13}C peaks at the 1930s level, although the overall profile is virtually constant. The profile for station 17 (Fig. 12C) appears to be an inverse of Core 10, a progressive increase in ^{13}C values downcore implying a decrease of terrestrial component downcore.

The nitrogen isotope records in all three cores (third panel, Figs. 12A-C) decrease downcore from heavier values to a relatively constant value below the mid 1960s. With this tracer, the decreases downcore were approximately the same, approximately 1.5‰. Del-^{15}N has been used with success in identifying sources of sedimentary (Coakley et al., 1992) and organic (van Dover et al., 1992) nitrogen. Del-^{15}N is also known to fractionate biologically (DeNiro and Epstein, 1981), becoming heavier as it moves into higher organisms.

The change in the ^{13}C of the sediment $CaCO_3$ is illustrated in the forth panel of Figs. 12A-C. Although there have been some species shifts in the foraminifera in the core from Core 10, Nelsen et al. (1994) report that Bulliminella morgani and Epistominella vitrea have been the predominant benthic foraminifera, averaging 42 and 23 % respectively of the total populations throughout its' length. Less than 5% of the biogenic carbonates could be attributed to pelagic foraminifera and virtually no non-biogenic carbonates were observed (Hood and Blackwelder, pers. comm.). Beginning around 1940, the ^{13}C of this carbonate material became lighter by approximately 0.6 ‰, with a similar change at station 2, but smaller at station 17. If primary production increased in the past century, we would expect to see lighter carbonate carbon as more isotopically light organic matter decomposed in the bottom waters and was incorporated into benthic foraminifera tests. The filled circles in the data for Core 10 are values for Bulliminella morgani sorted by Terri Hood.

Summary and Conclusions.

If benthic foraminifera population studies and glauconite abundance trends are viewed together, a coherent picture begins to emerge. These trends are temporally linked to known anthropogenic loading of fertilizer application (Fig. 11C) during this century (SAUS 1991-1975; Berry and Hargett, 1987). Thus, by inference they are linked to the resulting increases in nutrient flux down the Mississippi River (Bratkovich and Dinnel, 1992). Our working hypothesis is that the upcore increase in glauconite abundance, coupled with decreased benthic foraminifera species diversity, is related to anthropogenic forcing. Although benthic foraminifera were analyzed for only seven levels, a comparison of Fig. 11A vs. B indicates that the more diverse pre-1940's populations (mean SWDI = -1.06) coincides with low glauconite values. After the early-1940's, less diverse benthic foraminifera populations are reflected in a reduction in the SWDI (mean = -0.68). This upcore diversity decrease coincides with highly elevated glauconite abundance values. These transitions, at ~1940, temporally coincide with the inflection point for increase application of fertilizer in the United States. We propose that this relationship is the first evidence of linkage between the abundance of an authigenic phase (glauconite), biological species shifts, and an anthropogenic input factor.

Cores representing approximately 100 years of accumulation also have increasing concentrations of organic matter over this period, indicating increased accumulation of organic carbon, rapid early diagenesis, or a combination of these processes. Stable carbon isotopes and organic tracers show that virtually all of this increase is of marine origin. Evidence from three cores near the river mouth, two (stations 10 and 17) within the region of chronic seasonal hypoxia and one nearby but outside the hypoxic region (station 2) indicate that changes consistent with increased productivity began by approximately the mid-1950s when the inorganic carbon in benthic foraminifera rapidly became isotopically lighter at both stations. Beginning in the mid 1960s, the accumulation of organic matter, organic $d^{13}C$ and $d^{15}N$ all show large changes in a direction consistent with increased productivity. This last period coincides with a doubling of the load of nutrients from the Mississippi River which leveled off in the mid-1980s. These data, in conjunction with the foraminifera and glauconite data, support the hypothesis that anthropogenic nutrient loading has had a significant impact on the Louisiana shelf.

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